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GAS-PHASE PYROLYSIS OF SOME HYDROCARBONS IN FLOW SYSTEMS*

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INTRODUCTION

A series of studies on a variety of hydrocarbons has been undertaken to examine the kinetics of their thermal decomposition in flow systems. In the present work, previous studies of acetylene (1), diacetylene (2), and benzene (3) have been extended to methane, biphenyl, and, in a preliminary fashion, to naphthalene. Methane is considered to be of special interest because of the wealth of literature extant on its pyrolysis, and the conflicts in that literature; at the same time, the aromatic hydrocarbons are interesting because of the paucity of literature on them.

The experimental methods in all of this work have been similar. The apparatus has been described elsewhere. (2, 3) It consists essentially of a hot porcelain tube (5 mm i. d.) with a well-defined temperature plateau, through which hydrocarbon passes at low concentration in helium carrier gas. Analyses are performed by means of gas chromatography. In the studies of biphenyl and naphthalene, the entire inlet, outlet, and analytical systems have been kept at elevated temperature to avoid condensation of starting material.

We have made all calculations of residence times and rate constants on the basis of the temperature profiles as measured with a bare thermocouple under helium flow rates similar to those of the pyrolysis experiments. A detailed analysis of the possible errors due to errors in gas temperature, to lack of thermal equilibrium, or to lack of plug flow has not been carried out (for an excellent treatment of these effects, see Mulcahy and Pethard). (4) However, some calculations have been performed which indicate that such effects should not be important sources of error in this work. Therefore, we believe the rate behavior to be representative of the chemical kinetics of these substances.

RESULTS AND DISCUSSION

One of the hopes in this work has been to find similarities in behavior among some of the hydrocarbons. Therefore we group them, in the following discussion, according to their observed kinetic behavior.

Benzene, Biphenyl, and Naphthalene

In previous work on benzene (3) it was found that the kinetics over times of the order of 20×10^{-3} sec. could be described by mixed first- and second-order processes. The latter was thought to be a four-center reaction to form biphenyl and hydrogen. The first-order process was almost certainly a chain. Its rate was several orders of magnitude larger than any reasonable estimate of the rate of a bond-breaking reaction and its activation energy was low: of the order of 50 kcal. In order to account for the low activation energy it was postulated that one of the chain-carrying steps involved decomposition of phenyl radicals on the wall. It has since occurred to us that it might be possible also to have an important contribution from phenyl radical decomposition on carbonaceous nuclei, or incipient carbon particles, in the gas stream. These nuclei are formed very early, so the associated induction period would not be observed by our methods. Unfortunately, too little is known about the nucleation and growth of carbon particles to allow a quantitative kinetic treatment.

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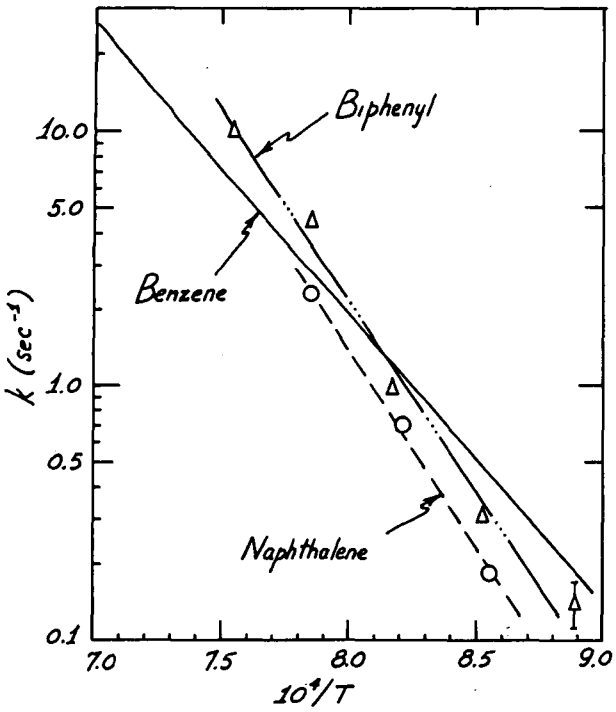

Fig. 1. First-order rate constants for thermal decomposition of benzene, biphenyl, and naphthalene in a flow system.

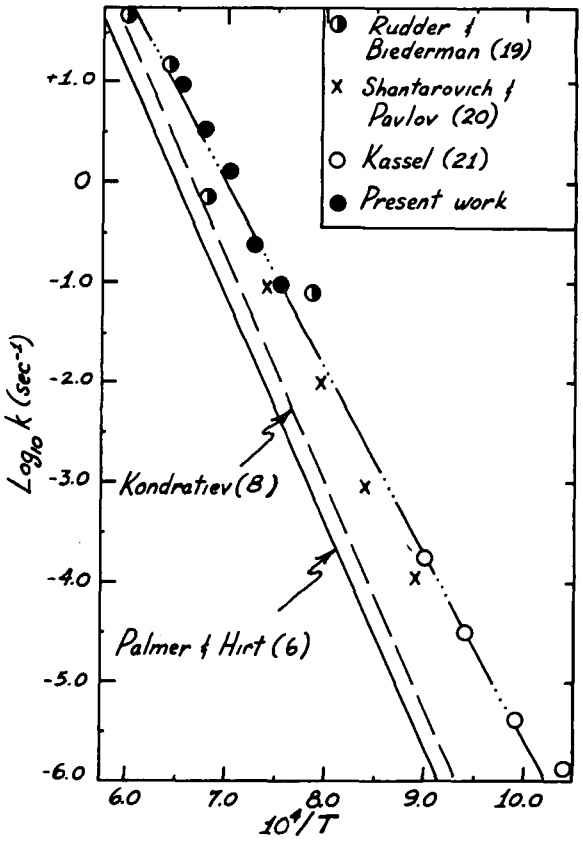

Fig. 2. First-order rate constants for thermal decomposition of methane in the low-temperature regime.

Our knowledge of the kinetics of biphenyl and naphthalene is even less extensive than the rather rudimentary data on benzene. In Figure 1 are presented the previously-determined first-order rate constants for benzene, (3) together with rate constants for biphenyl and naphthalene calculated on the assumption of first-order kinetics. The experimental tests for reaction order in the case of biphenyl have given ambiguous results. The order for naphthalene has not been tested. It is very probable that there is mixed-order behavior, as in benzene, in the case of both biphenyl and naphthalene. Kinney (5), in reviewing the pyrolysis of aromatic hydrocarbons, points out that reactions of the type

$$2(Ar)H \rightarrow (Ar)\text{-}(Ar) + H_2 \qquad (2)$$

occur in all three. Such reactions should be second-order.

However, in the absence of more detailed information, we prefer simply to make a first-order assumption for purposes of comparing rate behavior at comparable concentrations (ca. 1% by volume). Some support for this lies in the observation that benzene is produced from biphenyl in yields up to 20%. It cannot readily be formed in reactions of the type represented by equation 1. Figure 1 shows that between about 1100° and 1300°K, all three compounds decompose at roughly the same rate. Although lines have been drawn through the data, the temperature coefficients for biphenyl and naphthalene are not felt to be of sufficient accuracy to justify extrapolation. One can say that the similarity in rate constants is not surprising, and that they may well maintain similarity over a wide range of conditions. It is interesting to note that, if nucleation pehnomena do affect the rates, they too must be similar in all three.

Methane

The decomposition of methane should be completely understood by now. Having published the results of studies of the rate of deposition of carbon films from methane (6) that seemed to settle the question of the correct rate constant, we turned to the flow system for confirmation. To our dismay, we obtained the results shown in Figure 2, which agree very well indeed with the dozens of previous studies in flow and static systems. These have been reviewed by Kramer and Happel (7) and only three of them are shown in the figure. The line through the results from flow- and static-systems is expressed by

$$\log_{10} k = 13.0 - 18.6 \times 10^3/T \qquad (2)$$

corresponding to an activation energy of 85 kcal. This is to be compared with the result of Palmer and Hirt (6), based on their carbon deposition rates and shock tube studies:

$$\log_{10} k = 14.6 - 22.5 \times 10^3/T, \qquad (3)$$

corresponding to an activation energy of 103 kcal. Kondratiev's (8) recent result is nearly the same as equation 3.

It seems likely that these seemingly irreconcilable results actually express the behavior in two different kinetic situations. In the flow and static systems, residence times are relatively long and there is opportunity for nucleation to occur in the gas phase. These nuclei, which may be thought of as very large free radicals or as a highly dispersed solid with an extremely active surface, can promote direct decomposition of the methane. Tesner (9) has studied the direct decomposition of methane on carbon black (under the electron microscope). The process exhibits an activation energy equal to 78 kcal.

In shock tube studies, times are too short for nucleation, if it occurs at all, to have an appreciable effect. Our flow system studies overlap the temperature regime of Skinner's shock tube work. (10) The decomposition data at the two lowest temperatures (Figure 3) give indications of an induction period. However, even though our rate constants are based upon the decomposition at the shortest times (0.1-0.3 sec.), they are some 10 times greater than the shock tube results. That is, the induction period for the formation of nuclei seems (on the present hypothesis) to be essentially over before 0.1 sec. It is not at all difficult to imagine a rate that commences at the shock tube value and accelerates to the observed value in a time of the order of 0.1 sec. (or less, at the higher temperatures).

The deceleration at long times and large extent of decomposition (Figure 3) is probably due to back reactions. Since these may move not only carbon nuclei and hydrogen but also ethane, ethylene, and acetylene, no quantitative treatment is attempted.

The carbon film deposited on the wall during the pyrolysis of methane is of the vitreous carbon type, very different from carbon black. This is consistent with the low rate constants obtained from measurements of the rate of carbon deposition on the wall. (6) The film carbon seems to be inactive in promoting the direct decomposition of methane, and grows by decomposition of free radicals. Free radicals should also decompose on nuclei, but this should not

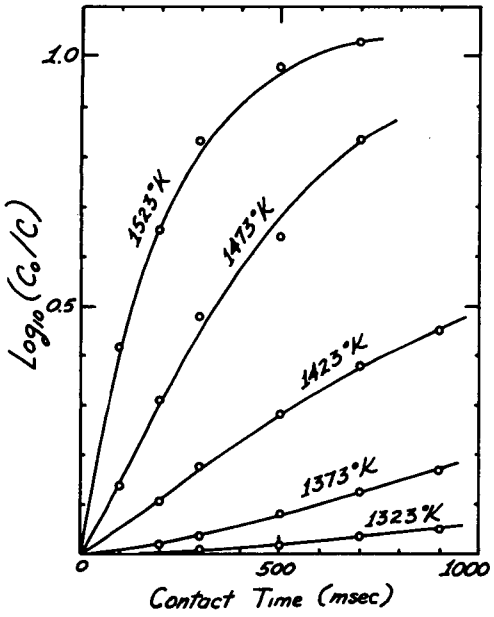

Fig. 3. Experimental data on thermal decomposition of methane in a flow system, at five temperatures.

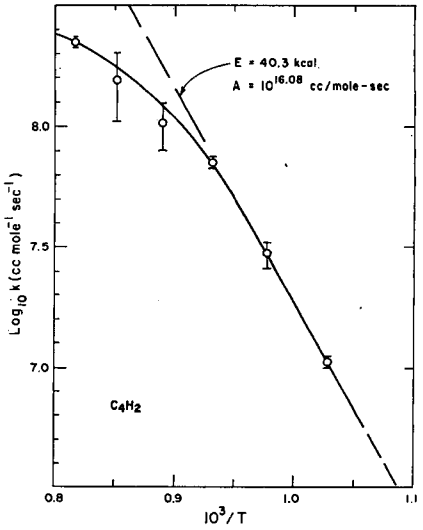

Fig. 5. Second-order rate constants for thermal decomposition of diacetylene in a flow system.

perturb the rate of wall deposition appreciably. The reason is that, at a typical (9,11) particle concentration of $3x10^{10}/cm^3$ and a diameter of 100A, the total surface area of the particles is less than 1% of the area of the reactor wall. Thus the rate of wall deposition should essentially equal the rate of creation of free radicals if they decompose on the wall with reasonable efficiency. A mathematical analysis of this process is presented elsewhere. (12)

We therefore still believe that equation 3 quite accurately represents the rate of the first step in the pyrolysis of methane. The question as to the identity of this step is still not settled, though it seems very likely that it is C-H bond rupture. The large pre-exponential factor in the rate constant is hardly compatible with splitting-out of H_2, whereas Skinner (10) has noted that it is quite reasonable if an H atom breaks off.

Acetylene and Diacetylene

We have no new experimental data to report on these compounds. There has, however, been some important new work on acetylene published by Gay, Kistiakowsky, Michael, and Niki (13) that deserves comment in the light of a previous study from our laboratory. (1) Gay et al (to be referred to as GKMN) used a time-of-flight mass spectrometer in a shock-tube study of the pyrolysis above 1600°K, and established the following:

(a) Isotopic exchange between C_2H_2 and C_2D_2 is much faster than the total pyrolysis reaction.

(b) The radical C_4H_3 is formed immediately and very rapidly reaches a steady state.

(c) The species C_4H_2, C_6H_2, and C_8H_2 form in that time sequence. C_4H_2 appears as early as C_4H_3.

GKMN note that all these species have been observed in sooting acetylene flames. (11) It may be significant that the species C_4H_4, which was not found by GKMN, has been identified in the flames.

GKMN then postulate the following mechanism to account for the rapid isotopic exchange:

$$2C_2H_2 \overset{k_1}{\rightleftarrows} C_4H_3 + H \qquad \Delta H_I = 46 \text{ kcal.}$$

$$H + C_2H_2 \overset{k_1}{\rightleftarrows} C_2H_3^* \rightarrow C_2H_2 + H \qquad \Delta H_2 = -39 \text{ kcal.}$$

They suggest that the pyrolysis occurs by reaction 1, followed by

$$C_4H_3 \cdot (+M) \overset{k_3}{\rightleftarrows} C_4H_2 + H \ (+M) \qquad \Delta H = 60 \text{ kcal.}$$

which gives diacetylene, followed in turn by reasonable steps to give higher species.

The second-order rate constants for pyrolysis thus are identified with k_1. GKMN point out that the mechanism is not flawless. We suggest here modifications that may render it more able to account for all the available evidence on acetylene pyrolysis. In this connection, there is some disagreement between ourselves and GKMN. They examined 76 rate constants from 10 publications, split them into two temperature regimes (620°-1000°K and 1000°-2450°K), formed least-squares Arrhenius expressions for these regimes and also for the whole collection, and observed that all three expressions agreed reasonably well. They concluded that a single rate constant probably governs the decomposition over the entire range, in contrast to our conclusion, from the same data, that there is a transition from long-chain behavior at low temperatures to non-chain behavior at low temperatures to non-chain behavior at high temperatures.

GKMN remark: "The large spread of reported activation energies is but a sad reflection of the difficulties in identifying an activation energy and a pre-exponential rate factor from a limited set of measurements." Our view is that the data on acetylene have nearly become unlimited, and critical attention to each work is necessary if one is to discover what is happening.

There are now some 96 rate constants available. We have plotted them in Figure 4, without attempting to use distinguishing symbols for individual publications. Shock tube data are, however, distinguished from flow- and static-system results. One can put a straight line through all points and obtain an activation energy of 40 kcal; or one can divide them in two, or in three. We have done the last, looking at the regions $10^4/T$ = 4-8, 8-12, and 12-16. These correspond approximately to the shock tube region, the flow system region, and the static vessel region.

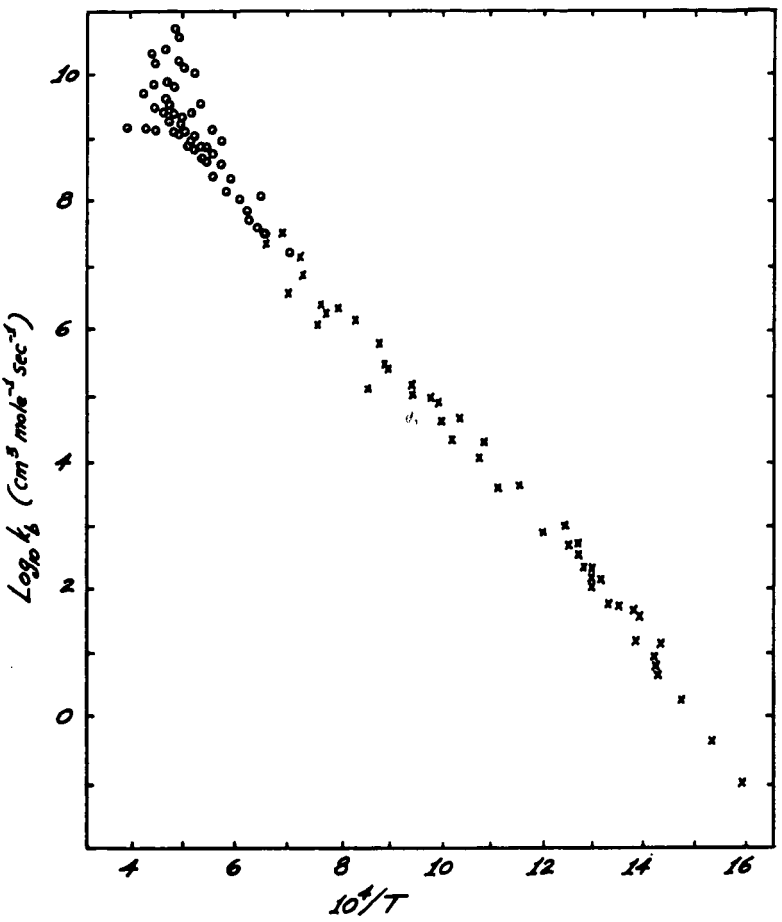

Fig. 4. Summary of all available second-order rate constants for thermal decomposition of acetylene. Circles are shock tube results.

One finds activation energies (excluding some obviously bad points from the shock tube region) of about 48 kcal, 35 kcal, and 48 kcal, respectively. These figures are compatible with transitional kinetic behavior.

However, there are other arguments that are more compelling:

(a) GKMN do not find C_4H_4 above 1600°K, and their mechanism does not provide for its formation. Nevertheless, the bulk of available evidence supports some mechanism that yields vinylacetylene, C_4H_4, as the first isolable product at low temperatures, with a shift to diacetylene, C_4H_2, at high temperatures.

(b) We are quite willing to accept GKMN's conclusion that the chain length in pyrolysis is of the order of unity at high temperatures; but at low temperatures the decomposition is a chain of considerable length (ca. 100).

(c) The "all points" activation energy of about 40 kcal does not appear to be compatible with the estimate (46 kcal) of the ΔH for GKMN's reaction 1. The situation worsens when one considers that the activation energy of the reverse reaction, $H + C_4H3 \rightarrow 2C_2H_2$, may be appreciable.

We think that a modification of the heuristic mechanism presented by Palmer and Dormish (1) can contribute to reconciliation of the various studies. In that mechanism there were five elementary reactions:

$$2C_2H_2 \rightarrow C_2H_2^* + C_2H_2 \qquad (I)$$

$$C_2H_2^* + C_2H_2 \rightarrow 2C_2H_2 \qquad (II)$$

$$C_2H_2^* + C_2H_2 \rightarrow C_4H_4^* \qquad (III)$$

$$C_4H_4^* + C_2H_2 \rightarrow C_4H_4 + C_2H_2^* \qquad (IV)$$

$$C_4H_4^* + C_2H_2 \rightarrow \text{products} \qquad (V)$$

The asterisk denotes a triplet state. For a discussion of the genesis of this mechanism, the interested reader can consult the original paper. (1) The point that we wish to make here is that reaction V may well be in competition with the unimolecular decomposition of C_4H_4*. For simplicity, let us assume that

$$C_4H_4^* (+M) \rightarrow C_4H_3 + H (+M) \qquad (VI)$$

provides the dominant competition, against reaction IV, for the species C_4H_4*. One notes that neither C_4H_3 nor H will continue the chain; but the H atom provides the necessary species for isotopic exchange, and provides it as soon as reaction commences. C_4H_3 decomposes rapidly at high temperature, yielding C_4H_2 and H, and exhibits a low steady-state concentration. It is possible that at low temperatures, C_4H3 extracts an H atom from some species and ends up as vinylacetylene.

Failure to observe C_4H_4 at high temperatures requires that its unimolecular decomposition have a large temperature coefficient. The problem of C_4H_4 seems to us to be the least satisfactory feature of the mechanism; but the experimental data are also somewhat unsatisfactory. Skinner and Sokoloski (14) found C_4H_4 in the products at 2000°K, but GKMN did not see it above 1600°K.

A steady-state treatment of the scheme (I-IV, VI) yields a second-order rate constant equal to

$$k_b = k_1(k_3/k_2)\{[3-k_4[C_2H_2]/(k_4[C_2H_2] + k_5)]/[1 + (k_3/k_2)k_5/(k_4[C_2H_2] + k_5)]\} \qquad (4)$$

Assuming $k_3 >> k_2$ at all temperatures, one finds that at low temperatures, where it is expected that $k_4 [C_2H_2] >>> k_5$,

$$k_b \simeq 2\ k_1\ (k_3/k_2) \qquad (5)$$

At high temperatures, where it is expected that $k_5 >>> k_4 [C_2H_2]$,

$$k_b \simeq 3k_1 \qquad (6)$$

These results at the temperature extremes are the same as were obtained before. (1) There is an interesting difference in the transitional behavior. The larger the concentration of acetylene, the higher the temperature necessary for the condition $k_5 >>> k_4 [C_2H_2]$. Comparison of experimental studies (1, 15, 16, 17) in the 900°K-1500°K region seems to indicate that the chain length does indeed remain moderately large in this region where $p_{C_2H_2}$ is 0.1 atm or more, while with partial pressures of the order of 10^{-2} atm, the reaction appears to have become essentially non-chain by about 1200°K. However, this conclusion is obscured slightly by the probable difference in the nucleation behavior at different concentrations.

As a final remark to connect the pyrolysis of diacetylene with that of acetylene, we reproduce the previously-reported (2) rate constants in Figure 5, and repeat the conclusion that the behavior seems to be very analogous to acetylene. There appear to be long chains at low temperatures and a transition towards non-chain behavior starting around 1100°K. A shock-tube study of C_4H_2 would be most welcome.

CONCLUSIONS

One can use tubular flow systems to gain some kinetic information of practical importance, and to gain some insight into probable mechanisms of decomposition of hydrocarbons. At sufficiently high temperatures, flow systems may yield quite accurate data on homogeneous processes if the rates of these are faster than nucleation rates. However, in such a temperature regime, the shock tube is apt to become a preferable tool. Alternatively, at lower temperatures one may be able to measure the rate of a process that is not affected by gas-phase nucleation. The rate of formation of a carbon film on the wall seems, albeit tentatively, to provide an independent technique of this type in the case of methane, and possibly in benzene. (18)

In the clarity of hindsight it is obvious that, in general, flow systems can yield fundamental data on homogeneous pyrolysis of hydrocarbons only if concentrations can be reduced to extremely low levels, to avoid nucleation problems. The alternative, and one much to be desired, is to use other devices (e. g. shock tubes) to study nucleation and particle growth in such detail that they can be introduced quantitatively into the analysis of flow system data.

LITERATURE CITED

(1) Palmer, H. B., and Dormish, F. L., J. Phys. Chem. 68, 1553 (1964).
(2) Hou, K. C., and Palmer, H. B., J. Phys. Chem. 69, 858 (1965).
(3) Hou, K. C., and Palmer, H. B., J. Phys. Chem. 69, 863 (1965).
(4) Mulcahy, M. F. R., and Pethard, M. R., Australian J. Chem. 16, 527 (1963).
(5) Kinney, C. R., The Chemistry of Petroleum Hydrocarbons, Vol. II., Brooks, B. T., Kurtz, S. S., Boord, C. E., and Schmerling, L., eds., Reinhold (1955), Chap. 26.
(6) Palmer, H. B., and Hirt, T. J., J. Phys. Chem. 67, 709 (1963).
(7) Kramer, L., and Happel, J., The Chemistry of Petroleum Hydrocarbons, Vol. II, Brooks, B. T., Kurtz, S. S., Boord, C. E., and Schmerling, L., eds., Reinhold (1955), Chap. 25.
(8) Kondratiev, V. N., Tenth Symposium (International) on Combustion, The Combustion Institute (1965), p. 319.
(9) Tesner, P. A., Seventh Symposium (International) on Combustion, Butterworths (1959), p. 546.
(10) Skinner, G. B., and Ruehrwein, R. A., J. Phys. Chem. 63, 1736 (1959).
(11) Bonne, U., Homann, K. H., and Wagner, H. Gg., Tenth Symposium (International) on Combustion, The Combustion Institute (1965), p. 503.
(12) Palmer, H. B., Carbon 1, 55 (1963).
(13) Gay, I. D., Kistiakowsky, G. B., Michael, J. V., and Niki, H., J. Chem. Phys. 43, 1720 (1965).
(14) Skinner, G. B., and Sokoloski, E. M., J. Phys. Chem. 64, 1952 (1960).
(15) Munson, M. S. B., and Anderson, R. C., Carbon 1, 51 (1963).
(16) Towell, G. D., and Martin, J. J., A. I. Ch. E. J. 7, 693 (1961).
(17) Cullis, C. F., and Franklin, N. H., Proc. Roy. Soc. (London) A280, 139 (1964).
(18) Murphy, D. B., Palmer, H. B., and Kinney, C. R., Industrial Carbon and Graphite, Society of Chemical Industry, London (1958), p. 77.
(19) Rudder, D., and Biederman, H., Bull. soc. chim. 47, 710 (1930).
(20) Shantarovich, P. S., and Pavlov, B. V., Zhur. Fiz. Khim. 30, 811 (1956).
(21) Kassel, L. S., J. Am. Chem. Soc. 54, 3949 (1932).